

Surface Chemistry

Supramolecular Polymer Brushes Grown by Surface-Initiated Atom Transfer Radical Polymerization from Cucurbit[7]uril-based Non-Covalent Initiators

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Abstract: Polymer brushes are densely grafted, chain end-tethered assemblies of polymers that can be produced via surface-initiated polymerization. Typically, this is accomplished using initiators or chain transfer agents that are covalently attached to the substrate. This manuscript reports an alternative route towards polymer brushes, which involves the use of non-covalent cucurbit[7]uril-adamantane host-guest interactions to surface-immobilize initiators for atom transfer radical polymerization. These non-covalent initiators can be used for the surface-initiated atom transfer radical polymerization of a variety of water-soluble methacrylate monomers to generate supramolecular polymer brushes with film thicknesses of more than 100 nm. The non-covalent nature of the initiator also allows facile access to patterned polymer brushes, which can be produced in straightforward fashion by drop-casting a solution of the initiator-modified guest molecules onto a substrate that presents the cucurbit[7]uril host.

Introduction

Polymer brushes are densely grafted, chain end-tethered assemblies of polymers that are anchored to a solid substrate.^[1–8] These thin polymer films are of interest for a variety of applications, as they allow to modify surfaces with a coating that, for example, can prevent biofouling^[9,10] or reduce friction.^[11] Polymer brushes can be prepared both via “grafting onto” and “grafting from” strategies.^[3,12,13] While the “grafting onto” strategy uses pre-synthesized, chain end-functionalized polymers that are tethered covalently or non-covalently to a substrate, the “grafting from” method involves growth of polymer brushes from substrates that are

modified with an appropriate polymerization initiator or chain transfer agent (CTA). Generally, the “grafting from” methodology allows access to densely grafted polymer brushes with film thicknesses of up to several hundreds of nanometers.^[12] The development of surface-initiated controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP),^[14,15] reversible addition-fragmentation chain-transfer polymerization (RAFT)^[16,17] and nitroxide-mediated radical polymerization (NMP)^[18,19] has facilitated the synthesis of polymer brushes with precisely defined film thicknesses and grafting densities, as well as polymer molecular weights, chemical composition, functionality and architecture.^[12,13]

Polymer brushes are generally grafted from solid substrates that present covalently attached initiators or CTAs. This results in densely grafted assemblies of polymers that are covalently anchored via their chain ends to the underlying substrate. The use of non-covalent chemistries to anchor polymerization initiators or CTAs to the substrate, and subsequently grow polymer brushes, in contrast, is much less explored. So far, only few examples have been reported of supramolecular polymer brushes that were grown via surface-initiated polymerization from substrates, which present initiators anchored via non-covalent interactions.^[20] In one example, pyrene-functionalized initiators were used to graft brushes from graphene.^[21] In another study, which also harnessed π - π interactions, supramolecular polymer brushes were grown from hydroxyl-functionalized self-assembled monolayers on silicon substrates that presented microcontact printed pyrene-based initiators.^[22] In addition to π - π interactions, also hydrogen bonding has been exploited to graft supramolecular polymer brushes. This has been demonstrated by mixing an ureido-pyrimidinone (UPy) functionalized macroinitiator with UPy-modified polycaprolactone to produce polycaprolactone films that present ATRP-initiators anchored via self-complementary quadrupole hydrogen bonds, which were used to grow poly(sulfobetaine methacrylate) brushes via ATRP.^[23]

A non-covalent strategy that has not yet been explored to graft supramolecular polymer brushes via surface-initiated polymerization involves the use of well-defined host-guest complexes to anchor polymerization initiators. In this study, as a first proof-of-concept, we explore the use of the ammonium adamantane@cucurbit[7]uril (Ada@CB[7]) host-guest complex to non-covalently immobilize initiators for surface-initiated atom transfer radical polymerization (SI-ATRP). CB[7] is a macrocyclic host molecule, and a

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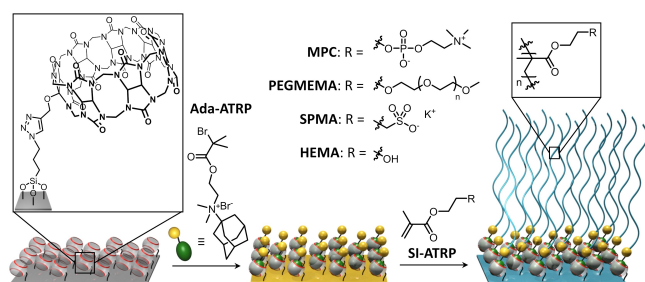
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homologue of the cucurbit[*n*]uril (CB[*n*]-family, which is able to form inclusion complexes in aqueous media with guests such as ferrocene and ammonium adamantane (Ada) derivatives that are characterized by very high binding constants ($\log K_a > 12$).^[24] This report demonstrates that the use of surface-bound, ATRP initiator-functionalized Ada@CB[7] host-guest complexes allows to generate supramolecular polymer brushes with dry film thicknesses of more than 400 nm. Furthermore, patterned supramolecular brushes can be produced via simple drop-casting of an aqueous solution of the ATRP initiator-functionalized adamantane derivative onto a CB[7]-modified substrate followed by SI-ATRP.

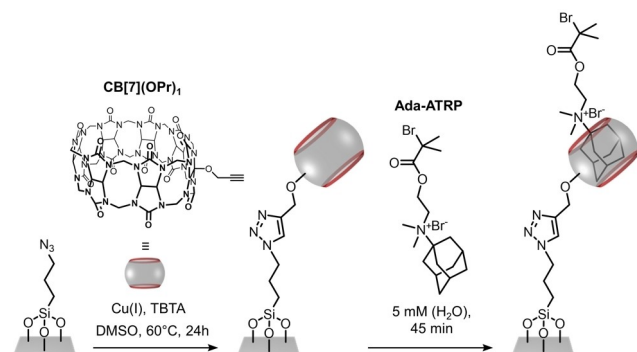
Results and Discussion

To investigate the feasibility of the Ada@CB[7] complex for the synthesis of supramolecular polymer brushes via surface-initiated polymerization, first, CB[7] moieties were covalently anchored to a silicon substrate. Following the formation of a surface-bound inclusion complex between the CB[7] host and a 2-bromoisobutyrate functionalized ammonium adamantane guest (Ada-ATRP), polymethacrylate brushes were grown via SI-ATRP (Scheme 1).

The first step towards exploring the Ada@CB[7] motif for the growth of polymer brushes via surface-initiated polymerization involves the modification of the substrate of interest, here a silicon wafer, with the supramolecular



Scheme 1. Synthesis of polymethacrylate brushes from supramolecular initiators tethered via Ada@CB[7] host-guest complexes.



Scheme 2. Synthesis of surface-immobilized ATRP initiator-functionalized Ada@CB[7] host-guest complexes.

initiator. Scheme 2 illustrates the strategy that was used to covalently anchor CB[7] moieties to the silicon substrate, and the subsequent formation of the Ada@CB[7] supramolecular complex on the surface. Silicon substrates presenting covalently anchored CB[7] receptors were obtained in two steps. First, oxygen plasma treated silicon substrates were modified with (3-azidopropyl)triethoxysilane, followed by copper-catalyzed azide-alkyne cycloaddition (CuAAC) with a monopropargyl-functionalized CB[7] derivative (CB[7](OPr)₁). The modification of the silicon substrates with CB[7] was monitored with X-ray photoelectron spectroscopy (XPS). Figure 1A presents C1s and N1s high resolution XPS scans recorded from a silicon substrate after modification with (3-azidopropyl)triethoxysilane, and subsequent coupling of CB[7](OPr)₁. The corresponding XPS survey spectrum is presented in Supporting Information Figure S1A.

The XPS spectrum confirms the successful surface immobilization of the CB[7] moieties. The C1s high resolution scan of the CB[7] modified surface can be fitted with 4 residuals. The areas of the residuals that can be assigned to the N-C-N and carbonyl carbon atoms (C=O) of CB[7] compare as N-C-N/C=O = 1.7:1, which is close to the expected N-C-N/C=O ratio of 2.0:1. Comparison of the areas of the C-C and C=O signals in the C1s high resolution scan indicates that 5.7% of the immobilized azido groups has reacted with CB[7](OPr)₁. Taking a surface area of 20 Å² per molecule for (3-azidopropyl)triethoxysilane^[25] and of 200 Å² for CB[7],^[24] this corresponds to ~70% of the maximum possible CB[7] surface concentration assuming a perfect hexagonal packing of the surface-anchored CB[7] moieties. The N1s high resolution scan of the CB[7] functionalized surface can be resolved into two peaks, a larger signal due to the NR₃ nitrogen atoms, and a small shoulder at higher binding energies, which can be assigned to the N-N-N nitrogen of the triazole group, contributing to 2.7% of the total N1s area (3.2% expected).

Prior to the immobilization of Ada-ATRP on silicon substrates modified with the covalently anchored CB[7]

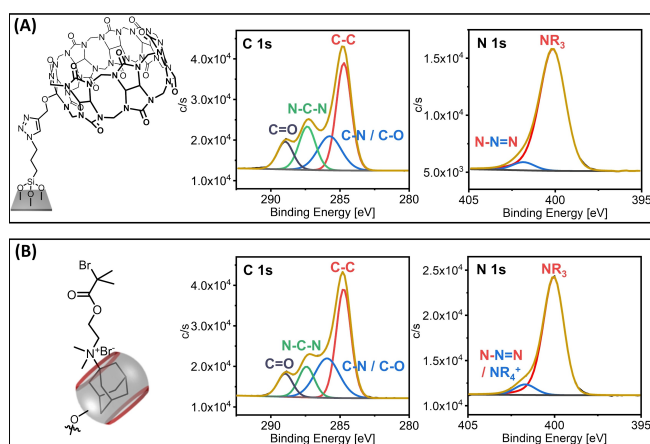


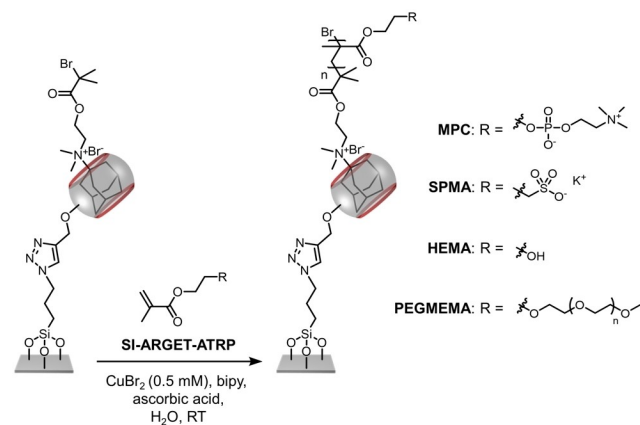
Figure 1. Chemical structure, C1s and N1s high resolution XPS scans of (A) a CB[7](OPr)₁-functionalized silicon surface, and (B) an Ada-ATRP@CB[7]-functionalized silicon surface.

moieties, the host–guest complex formation between this adamantane derivative and CB[7] was studied by solution ^1H NMR spectroscopy (Supporting Information Figure S2). The ^1H NMR spectrum of the host–guest complex revealed a high-field shift of the adamantane resonances, which is characteristic for the formation of the Ada@CB[7] host–guest complex.^[26] This is important as it confirms that complex formation between Ada-ATRP and CB[7] involves binding of the adamantane moiety, and not the ATRP initiator, to the CB[7] cavity. To form surface-anchored supramolecular Ada-ATRP@CB[7] host–guest complexes, a CB[7]-modified silicon wafer was immersed into a 5 mM aqueous solution of Ada-ATRP for 45 min. C1s and N1s high resolution XPS spectra and survey scans of the surface-bound ATRP initiators are shown in Figure 1B and Supporting Information Figure S1B, respectively. Binding of Ada-ATRP is evidenced by changes in the relative ratios of the C=O, N–C–N, and C–N/C–O C1s residuals. Furthermore, the N1s high resolution scan again can be resolved in two residuals, however, with the highest binding energy component at 401.6 eV now including the contributions of two components, viz. the N–N=N nitrogen of the triazole moiety, as well as that of the quaternary ammonium group in Ada-ATRP. The relative ratio of the areas of the two N1s residuals is 24:1 (expected 15:1), which indicates that 63 % of the surface-bound CB[7]-molecules have formed a host–guest complex with Ada-ATRP. To further proof the formation of the surface-bound Ada@CB[7] complex, a fluorescein-labeled ammonium-adamantane derivative was synthesized (Ada-Flu). The ability of Ada-Flu to form host–guest complexes with CB[7] was also confirmed by solution ^1H NMR spectroscopy (Supporting Information Figure S3). The ^1H NMR spectrum of the Ada-Flu@CB[7] host–guest complex reveals high field shifts similar to those observed for the Ada-ATRP@CB[7] complex, indicative of the binding of the adamantane moieties by the CB[7] host. To demonstrate the formation of surface-bound Ada@CB[7] complexes, a CB[7] modified silicon substrate was immersed in a 100 μM aqueous solution of Ada-Flu, and subsequently rigorously rinsed with water (see Supporting Information). Fluorescence microscopy analysis of the substrate revealed a green fluorescence reflecting the formation of the surface-bound Ada-Flu@CB[7] complex, whereas no fluorescence could be detected on a control substrate that had not been immersed in a solution of Ada-Flu. (Supporting Information Figure S4).

One important factor that drives the formation of, and contributes to the stability of, CB[n]-based host–guest complexes is the release of high-energy water molecules that are expelled from the CB[n] cavity upon guest binding.^[24] In non-aqueous media, such as for example DMSO or acetonitrile, the binding constants of CB[n] complexes have been estimated to be up to 8 orders of magnitude lower.^[27] As a consequence, to explore the feasibility of the surface-anchored Ada-ATRP@CB[7] initiators to generate supramolecular polymer brushes, polymerization experiments were conducted in aqueous media with four different water-soluble monomers, viz. 2-methacryloyloxyethyl phosphorylcholine (MPC), 3-sulfopropyl methacrylate potassium

salt (SPMA), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), and 2-hydroxyethyl methacrylate (HEMA) (Scheme 3).

These monomers were polymerized using an activators regenerated by electron transfer (ARGET) ATRP protocol that uses CuBr_2 , 2,2'-bipyridine (bipy), and ascorbic acid.^[28] Growth of the polymer brushes was monitored by measuring the dry film thickness as a function of polymerization time. Figure 2A presents the results of SI-ARGET-ATRP experiments that were performed with MPC at monomer concen-



Scheme 3. Synthesis of polymer brushes via SI-ARGET-ATRP from surface-immobilized Ada-ATRP@CB[7] supramolecular initiators.

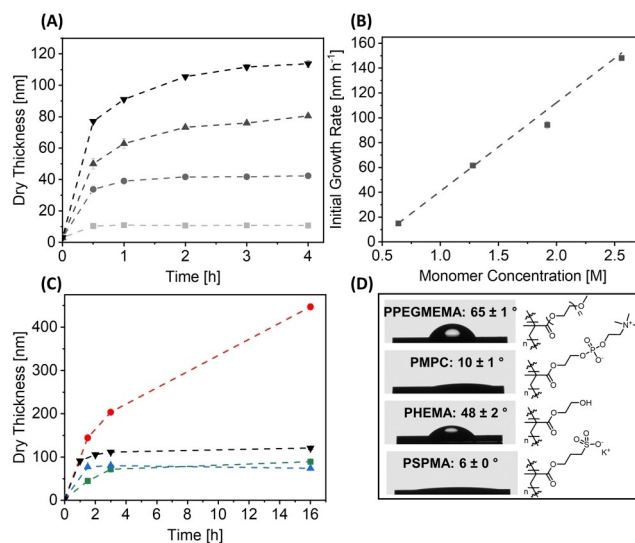


Figure 2. (A) Evolution of dry film thickness of PMPC brushes as a function of polymerization time for syntheses carried out at monomer concentrations of 0.64 M (■), 1.28 M (●), 1.92 M (▲) and 2.56 M (▼); (B) Monomer concentration dependence of the initial film growth rate for SI-ARGET ATRP of MPC performed at different monomer concentrations; (C) Film growth profiles (dry film thickness as a function of polymerization time) for PPEGMEMA (●), PMPC (▼), PHEMA (■) and PSPMA (▲) brushes prepared by SI-ARGET-ATRP using a monomer concentration of 2.56 M; (D) Chemical structures and water contact angles of PPEGMEMA, PMPC, PSPMA, and PHEMA brushes (dry film thicknesses of the brushes were: PPEGMA = 450 nm; PMPC = 80 nm; PSPMA = 74 nm, and PHEMA = 90 nm).

trations of 0.64, 1.28, 1.92 and 2.56 M over a period of 4 h. The film growth profiles shown in Figure 2A are reminiscent of those typically reported for covalently tethered brushes generated by SI-ATRP.^[29,30] In the initial stages of the polymerization process, a rapid, typically linear increase in dry film thickness with polymerization time is observed, which is characteristic of the controlled nature of the ATRP process. This is then followed by a gradual decrease in the film growth rate, i.e. polymerization rate, and a levelling off towards a plateau dry film thickness. The latter reflects the loss of polymerization active chain ends as the polymerization reaction proceed. The data in Figure 2A indicate a gradual increase both in the initial rate of polymerization as well as in the plateau dry film thickness upon increasing the monomer concentration from 0.64 M to 2.56 M. Using a monomer concentration of 0.64 M, PMPC brushes with thicknesses of up to 10.8 ± 0.6 nm could be obtained. Increasing the monomer concentration to 1.28 M, 1.92 M and 2.56 M allowed to generate PMPC brushes with maximum dry film thicknesses of 42.4 ± 0.3 nm, 80.5 ± 0.8 nm, and 113.7 ± 2.2 nm, respectively. All measured film thicknesses are also listed in Supporting Information Table S1. Analysis of the initial stages of the film growth profiles that are presented in Figure 2A allows to estimate the film growth rates at the different monomer concentrations. Figure 2B plots the film growth rates that were obtained by considering the first 30 min of the polymerization reaction as a function of monomer concentration. This analysis reveals a linear dependence of the film growth rate on monomer concentration, which has also been observed in other experimental studies using covalently attached initiators, and predicted by theory.^[31,32]

To estimate the grafting density of the supramolecular brushes, the swelling behaviour of a PPEGMEMA brush with a dry film thickness of 83.0 ± 4.4 nm in water was investigated by ellipsometry. The resulting swollen film thickness and swelling ratio were analysed both using the self-consistent field theory developed by Milner et al., as well as following the Alexander–de Gennes theory to afford grafting densities of 0.031 chains/nm², respectively 0.014 chains/nm² (see Supporting Information).

The SI-ARGET-ATRP experiments discussed above were conducted using 0.5 mM Cu^{II}Br₂ and 6 mM bipy in the presence of 14 mM ascorbic acid. Supramolecular PMPC brushes could also be grown using conventional conditions with Cu^I/bipy as the catalyst system. The use of these polymerization conditions, however, resulted in a significant decrease in dry polymer brush film thickness as compared to the use of SI-ARGET-ATRP. For example, after 1.5 h reaction time, SI-ARGET-ATRP of MPC at a monomer concentration of 2.56 M resulted in supramolecular PMPC brushes with a film thickness of 98.1 ± 2.9 nm. In contrast, when the Cu^IBr/bipy catalyst system was used at the same monomer concentration, SI-ATRP of MPC afforded brushes with dry film thicknesses of 37.5 ± 2.6 nm and 20.3 ± 1.2 nm, for [Cu^I]=8 mM and 21 mM, respectively (Supporting Information Figure S5 and Supporting Information Table S2). The decrease in film thickness that was observed when catalyst systems that operate at high concentrations of

copper salt were used can be attributed to partial decomplexation of the surface-attached Ada@CB[7] host–guest complexes.^[32–35] This results in a decrease in the ATRP initiator surface concentration, and thus grafting density, and as a consequence a decrease in dry film thickness for brushes prepared at identical polymerization times.

After demonstrating the use of the surface-anchored Ada-ATRP@CB[7] host–guest complex to initiate growth of PMPC brushes, further experiments were conducted with PEGMEMA, HEMA and SPMA as monomers. Figure 2C (Supporting Information Table S3) compares the evolution of the dry ellipsometric film thickness of polymer brushes obtained from these three monomers and of MPC for SI-ARGET-ATRP experiments that were performed over a period for up to 16 h, and that used a monomer concentration of 2.56 M. Under these conditions, PSPMA, PHEMA and PPEGMEMA brushes with dry thicknesses of up to 73.5 ± 1.7 nm, 89.3 ± 1.7 nm, and 447.0 ± 5.9 nm respectively could be prepared. The supramolecular polymer brushes were characterized by XPS and water contact angle analysis. XPS spectra of the brushes are included in Supporting Information Figure S6, and agree with the chemical structure of the polymers. Figure 2D presents results of water contact angle analysis of the brushes, which are in agreement with literature values.^[36–39] Supramolecular PPEGMEMA brushes could also be prepared using conventional ATRP instead of ARGET-ATRP conditions. As it was also observed for the surface-initiated polymerization of MPC, this resulted in a substantial reduction of the dry polymer brush film thickness (Supporting Information Figure S5). For example, for a polymerization time of 1.5 hrs, PPEGMEMA brushes with dry film thicknesses of 87.8 ± 3.8 nm and 56.0 ± 2.4 nm were obtained when conventional ATRP conditions with [Cu^I]=8 mM and 21 mM were used, as opposed to 144.5 ± 4.2 nm when ARGET-ATRP conditions were applied.

The non-covalent immobilization of the ATRP initiator also provides a facile route towards patterned polymer brushes without the need for, for example, photo- or electron beam lithography.^[12,13] Patterned supramolecular brushes can be obtained via simple drop casting of an aqueous solution of Ada-ATRP onto a CB[7] modified substrate (Figure 3A). As a first proof-of-principle, a 30 μ L droplet of a 1 mM aqueous solution of Ada-ATRP was placed on a CB[7](OPr)₁-modified wafer. After rinsing the substrate with water, PEGMEMA was polymerized using ARGET-ATRP conditions for 2.5 h. Figure 3B shows a photographic image of a wafer with the patterned PEGMEMA brush. The image shows a sharp boundary between the Ada-ATRP-modified (yellow/gold) and non-modified (grey) areas on the surface. The corresponding ellipsometry map, which was constructed from the measurement of 35 points across the whole wafer, is shown in Figure 3C and indicates a dry PEGMEMA brush thickness of 187.3 ± 11.9 nm. The ellipsometry map in Figure 3 also reveals the presence of a 14.3 ± 2.2 nm thick film on the area of the substrate that was not patterned with the Ada-ATRP initiator. XPS analysis of the unmodified side (Supporting Information Figure S7) reveals a thin layer of PPEGMEMA.

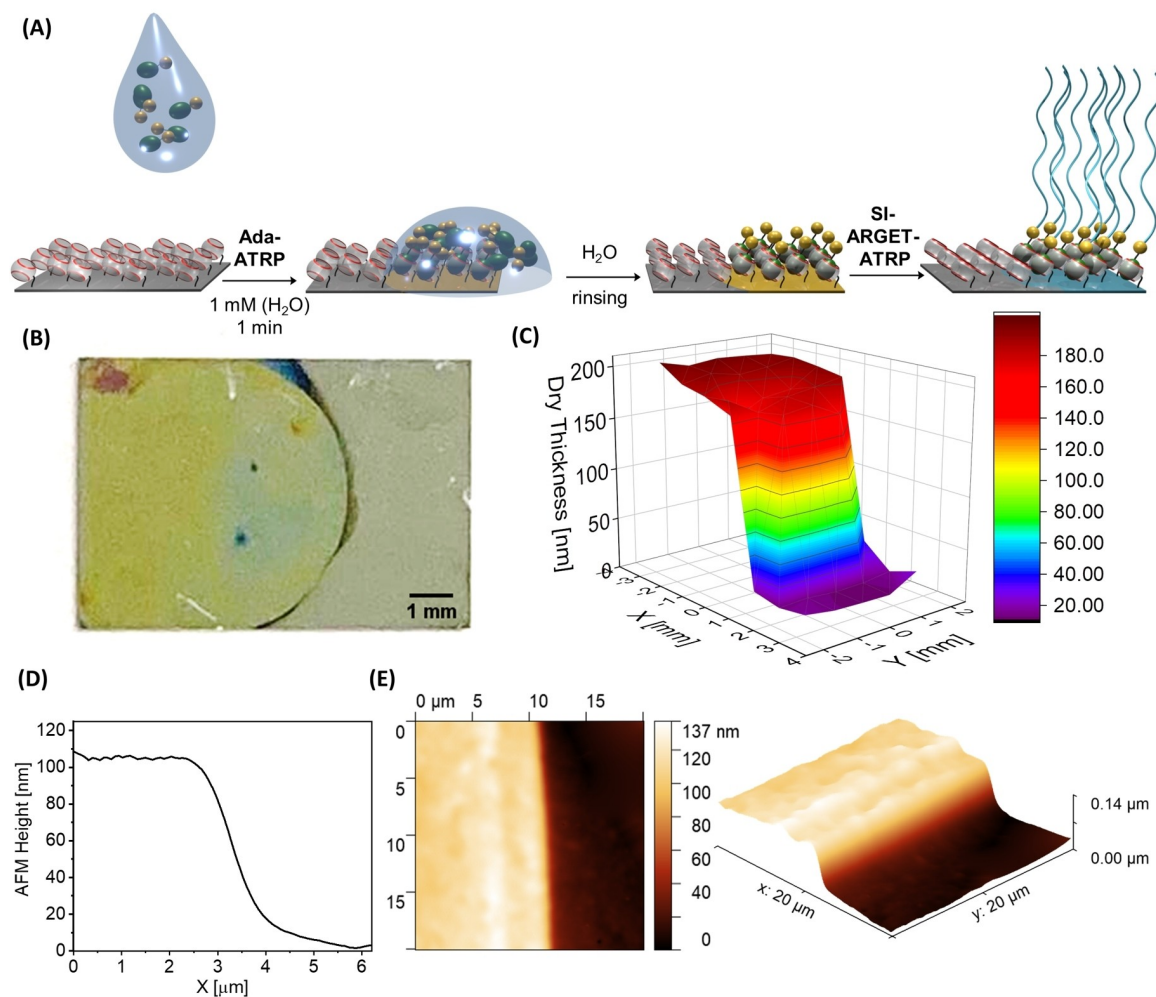


Figure 3. (A) Preparation of patterned non-covalent PEGMEMA brushes via drop-casting of Ada-ATRP on a CB[7]-modified substrate; (B) Image of a 5.5×8 mm silicon wafer (light grey) with patterned PEGMEMA polymer brushes (gold). (C) Topographical map of the whole patterned wafer obtained with ellipsometry showing a PEGMEMA film thickness 187 ± 12 nm and a measured film thickness of 14 ± 2 nm in the unmodified area; (D) Height profile of the border region between the polymer brush bearing side and unmodified side, obtained with AFM; (E) 2D (left) and 3D (right) AFM-image of the border region between the polymer brush bearing side and unmodified side.

The formation of the thin polymer film in the non-patterned areas is attributed to physisorption of PEGMEMA or solution polymerized PEGMEMA. This was confirmed in a control experiment in which a wafer bearing CB[7](OPr)₁ was exposed to the same polymerization conditions without previous exposure to Ada-ATRP. After 2 h, the wafer was rinsed with water, dried and analyzed with ellipsometry. This revealed a film thickness of 12.9 ± 1.0 nm, which is similar to that found in the non-modified part of the patterned wafer. Taken together, the results presented in Figure 3 demonstrate that the use of non-covalent initiators provides a facile strategy for the preparation of patterned polymer brushes.

While there have been some efforts to explore supramolecular approaches to chain end tether polymer grafts to solid surfaces, both via the grafting-from strategy that is presented here, as well as via grafting-onto approaches,^[20] comparably little is known about the thermodynamics and kinetics of these interactions at solid surfaces

and the stability of the resulting supramolecular polymer brushes. In a first attempt to obtain insight in the formation of surface-bound Ada@CB[7] host-guest complexes, a silicon substrate presenting surface-anchored CB[7] moieties was presented with a series of Ada-Flu solutions covering a range of concentrations from 0.23 to $7.5 \mu\text{M}$. After washing, the substrates were imaged with fluorescence microscopy, and the fluorescence intensities that were determined analyzed using a Langmuir isotherm (Supporting Information Figure S8). This afforded a binding constant of $\log K_A = 6.6 \pm 5.0$. While the uncertainty in the binding constant is high (which we attribute to the very high affinity of CB[7] for the adamantane host), the concentration dependence of the measured fluorescence intensity is characteristic for the formation of host-guest complexes. The results presented in Supporting Information Figure S8 also demonstrate that the use of non-covalent interactions provides a facile strategy to vary the surface-concentration of surface-bound Ada, and thereby to control the grafting density of the polymer

brushes. Next, supramolecular PMPC and PSPMA brushes were incubated in different solvents, and the dry film thickness monitored to evaluate dissociation of the host–guest complexes, and detachment of the polymer grafts. These experiments were performed in solvents that are (good) solvents for the polymers (water and DMSO) as well as in toluene, which is poor solvent for the polymer but destabilizing for the Ada@CB[7] complex. In toluene and DMSO no changes in dry film thickness were observed over a period of 24 h (Supporting Information Figure S9). Incubation of a PMPC brush in a large (10 L) volume of water that was replaced daily for up to 16 days, however, resulted in an ~50% decrease in dry film thickness (Supporting Information Figure S9). This indicated a 50% reduction in grafting density, i.e. a detachment of ~50% of the initial surface-anchored PMPC grafts. This is less as what would be expected based on the Langmuir isotherm model. We attribute this to the steric barrier imposed by the polymer brush layer, which hinders diffusion of polymer chains in the decomplexed state away from the surface and out of the polymer brush. The time scale of these diffusion processes is likely to be much larger (and rate determining) as compared to the rates for the reversible formation and decomplexation of the surface-bound host–guest complexes. The results of these experiments are in line with observations reported earlier on supramolecular polymer brushes that were prepared via grafting-onto approaches,^[40,41] and indicate that the formation and stability of supramolecular polymer brushes are determined by a multitude of intricate factors that include the polymer molecular weight, grafting density and chemical composition, as well as the nature of the host–guest complex (and its binding constant) and the solvent used. This study has demonstrated the use of well-defined host–guest complexes to anchor initiators for the growth of polymer brushes via surface-initiated polymerization, and pointed towards key parameters that can be used to tune the responsiveness/reversibility of these supramolecular brushes.

Conclusion

This study has demonstrated the use of the cucurbit[7]uril-adamantane host–guest motif to prepare non-covalently surface-immobilized initiators for atom transfer radical polymerization. These non-covalent initiators have been successfully used for the surface-initiated atom transfer radical polymerization of 4 different water soluble methacrylates, and allowed the synthesis of supramolecular polymer brushes with dry film thicknesses of more than 100 nm. Drop-casting an adamantane-functionalized ATRP initiator onto a surface presenting the cucurbit[7]uril host allows to prepare patterned initiator modified surfaces without the need for lithographic tools, and enables the synthesis of patterned supramolecular polymer brushes. The surface concentration of the CB[7]-bound Ada can be easily tuned, which provides a straightforward approach to vary the polymer brush grafting density. The work presented here also reveals that the stability of supramolecular

polymer brushes is determined by a multitude of intricate factors including polymer molecular weight, grafting density and chemical composition, as well as the nature of the host–guest complex (and its binding constant) and the solvent. Careful control of these parameters will allow to tune the responsiveness/reversibility of these supramolecular brushes. The ability to produce supramolecular polymer brushes via surface-initiated polymerization provides further opportunities, for example, towards lubrication surfaces capable of self-repair.^[20,42]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Atom Transfer Radical Polymerization · Cucurbituril · Host-Guest Systems · Polymers · Surface-Initiated Polymerization

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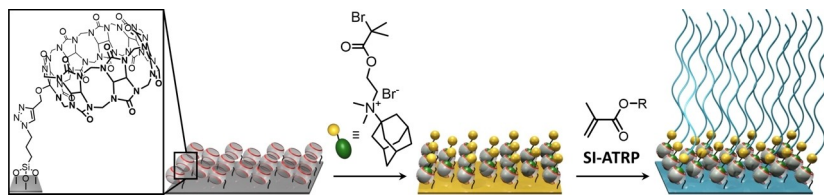
Research Articles

Surface Chemistry

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Supramolecular Polymer Brushes Grown by Surface-Initiated Atom Transfer Radical Polymerization from Cucurbit[7]uril-based Non-Covalent Initiators



Surface-immobilized, initiator-modified cucurbit[7]uril (CB[7])-adamantane host-guest complexes allow the growth of supramolecular brushes with thicknesses of > 100 nm via atom transfer radical polymerization. The non-covalent

immobilization of the initiator also provides a facile route towards patterned polymer brushes via drop casting of an aqueous solution of an initiator-modified adamantane derivative onto a CB[7] functionalized substrate.